Gas Separation Hot Paper

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Porous Liquids: A Promising Class of Media for Gas Separation[**]

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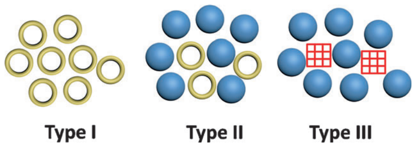
Abstract: *A porous liquid containing empty cavities has been successfully fabricated by surface engineering of hollow structures with suitable corona and canopy species. By taking advantage of the liquid-like polymeric matrices as a separation medium and the empty cavities as gas transport pathway, this unique porous liquid can function as a promising candidate for gas separation. Moreover, such a facile synthetic strategy can be further extended to the fabrication of other types of nanostructure-based porous liquid, opening up new opportunities for preparation of porous liquids with attractive properties for specific tasks.*

Porous liquids with permanent nanopores are of considerable fundamental interest because of the incorporation of empty cavities into the dense liquid state, which can bring novel functionality to conventional liquids for a variety of applications.[1] Scheme 1 shows three classes of porous liquids that have been proposed by James et al. based on the nature of the host systems.[1a] For example, Type I is a neat liquid composed of fluid hosts with empty cavities, while Type II and Type III are essentially dissolved empty hosts in sterically hindered solvents or homogeneously dispersed framework materials in hindered solvents, respectively. Until now, several synthetic approaches to create porous liquids have been proposed,[1a] and some have been adopted in the laboratory, such as the extension of the chain length of molecular cages[2a] or the dispersion of microporous frameworks in organic solvents.[2b,c] However, these methods can suffer from some difficult issues during sample preparation,[3] including intermolecular self-filling, easy collapse or decomposition of the organic hosts and serious settling of nanoparticles, making the fabrication of stable porous liquids a significant challenge.



Scheme 1. Three classes of porous liquids based on the properties of the host systems (adapted from Ref. [1a]).

Surface engineering of nanoparticle cores with organic corona-canopy species (generally oligomers or polymers) by ionic or covalent grafting has been well established by Giannelis et al. for the production of solvent-free nanofluids.[4] In this hybrid system, the polymeric canopy acts as a fluid medium resulting in liquid-like behavior, while the core nanoparticles can be varied from oxides (e.g. SiO_2, ZnO) to metals (e.g. Pt, Au), carbons (e.g. carbon nanotubes, graphene) and even to DNA molecules.[4,5] The high flexibility and compatibility of this synthetic strategy enables broad tunability of the hybrid systems with desired functionality for specific applications.[4b,c] For instance, optimizing the chemical structure of the organic canopies can efficiently enhance gas absorption and selectivity towards CO_2;[6a–c] while selecting FePt or CdSe/CdS/ZnS nanoparticles as cores can create additional function in the nanofluids, such as magnetism and luminescence.[6d,e] In this regard, it is highly desirable to fabricate porous liquids by the surface engineering of porous structures with liquid-like polymeric canopies.

Herein, a Type I porous liquid based on hollow silica spheres is designed and fabricated in a two-step synthetic procedure (Scheme 2).[4] To preserve the hollow structures in the liquid state, it is necessary to prevent the fluid medium from self-filling the cavities. Toward this end, hollow silica (HS) spheres with microporous shells that essentially function as molecular sieves by blocking species larger than 1.9 nm were first synthesized as the core particle;[7] while a positively charged organosilane (OS) moiety with molecular size approximately 2.0 nm was used as the corona for surface modification (Figure S1 in the Supporting Information).[5a] Experimentally, in the first step, OS selectively reacts with hydroxy groups bound to the silica shell surface leading to a permanent, covalent attachment of a corona onto the hollow particles (denoted by OS@HS). The chloride counteranion balancing the positively charged corona was then replaced by a negative poly(ethylene glycol)-tailed sulfonate (PEGS) canopy, yielding an optically transparent hollow-silica porous liquid (denoted as HS-liquid) at room temperature. In such organic–inorganic hybrid fluids, the hollow particles are homogeneously combined with an organic

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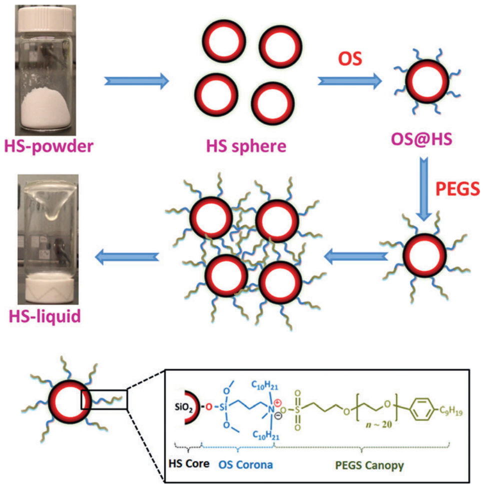

Scheme 2. Two-step synthetic strategy for porous liquid fabrication. HS = hollow silica, OS = organosilane.

suspending medium (corona–canopy species) into one homogeneous system, which is quite distinct from that of conventional colloidal suspensions, where the particles and solvents are physically distinct entities.[4b] Benefiting from such a unique arrangement, the resultant HS-liquid should be extremely stable at room temperature.[4]

In Figure 1 a, the synthetic steps of the HS-liquid are examined by Fourier-transform infrared (FT-IR) spectra. For the starting HS powder, the characteristic bands (1050 cm^{-1} and 800 cm^{-1}) of the Si-O-Si vibration modes are clearly observed, indicating the successful evolution of a silica framework from the silane precursors.[8a] In addition, the absorption peak at 3400 cm^{-1} can be attributed to the stretching vibrations of structural hydroxy groups bound on silica shells.[8a] Chemically, these surface-bound hydroxy groups are critical for the porous-liquid fabrication, serving as the reactive sites for corona grafting.[5] After surface modification, some featured bands assigned to the OS moiety are clearly visible in the OS@HS spectrum, such as the stretching and bending vibrations of -CH$_2$- backbones at 2920 cm^{-1}, 2840 cm^{-1} and 1470 cm^{-1}.[8b] More importantly, the absorption originating from the Si-O-Si stretching is further enhanced at 1050 cm^{-1}, accompanied by the disappearance of Si-O-C vibration at 1084 cm^{-1} and 1033 cm^{-1} for the OS moiety (Figure S2 a).[8c] In addition, the ratio of the Si-OH signal to that of Si-O-Si decreases from 8.2 % for HS to 3.6 % for OS@HS (see Figure S2 b), suggesting that the increase of the Si-O-Si absorption peak intensity is due to the surface reaction between Si-OH and Si-O-C rather than self-condensation of the OS. Hence, the OS corona is chemically bound on the HS surfaces, rather than just physically coated. To confirm that the hollow structure remained empty after OS modification, OS@HS was also characterized by transmission electron microscopy (TEM) and N$_2$-sorption isotherms. In Figure S3, well-defined hollow spheres are clearly observed for OS@HS, indicating that OS is blocked by the microporous shells. Moreover, there was no significant change in the N$_2$ adsorption isotherm shape for OS@HS, which suggests that the hollow frameworks are well preserved after surface modification (Figure 1 b) in agreement with TEM observations. This finding is rather important, it demonstrates that the empty cavities of OS@HS can be still accessible by gas molecules. In the spectrum of the HS-liquid, additional bands characteristic of ether (1105 cm^{-1}), aliphatic (2874 cm^{-1}), phenyl (1651 cm^{-1}), and sulfonate (1205 cm^{-1}) groups are clearly seen,[5a] suggesting that the OS-modified hollow spheres are entirely surrounded by the PEG-containing canopy to afford a liquid-like behavior.

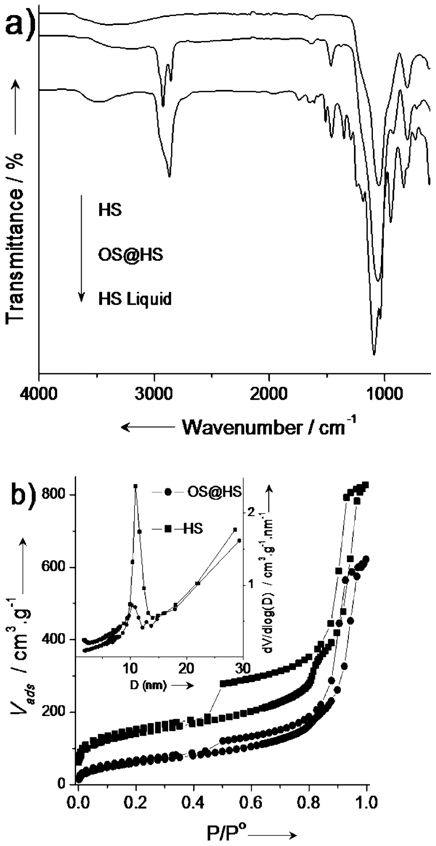

Figure 1. a) FT-IR spectra of HS, OS@HS, and HS-liquid, b) N$_2$-asorption isotherm of HS and OS@HS. Inset: Pore size distributions calculated with the Barrett–Joyner–Halenda (BJH) method.

Figure 2 a displays the thermogravimetric analysis (TGA) of the HS-liquid. There is no evident mass loss during heating until the temperature reaches approximately 260 °C, demonstrating that the HS-liquid is solvent-free.[5a] The thermal decomposition of the HS-liquid starts at 260 °C and finishes at 370 °C, corresponding to the pyrolysis of organic groups bound on the HS surfaces. At a temperature of approximately 600 °C, the final residual mass of the inorganic hollow spheres is determined as 17.5 %. Assuming a uniform surface coverage, an average of four corona–canopy chains is calculated per square nanometer of hollow sphere surface. In conclusion, the thermal stability of the HS-liquid is closely dependent on the organic building blocks.

The glass–liquid phase transition of the HS-liquid was studied by differential scanning calorimetry (DSC) analysis. Upon heating from −80 °C, an exothermic second-order transition at −55 °C is observed, which corresponds to the glass transition (T_g).[5] It should be noted that a crystallization peak for the HS-liquid occurs at −6 °C, as indicated by the

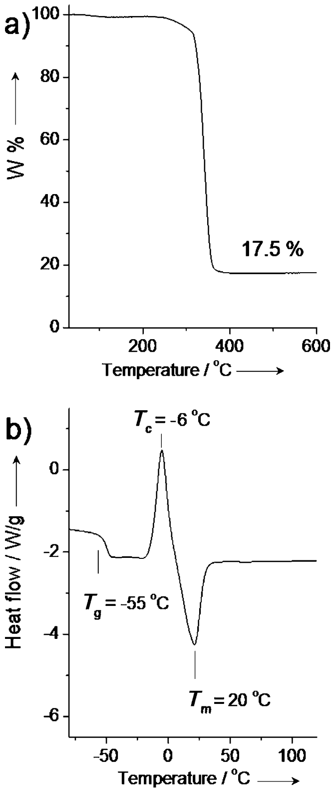

Figure 2. a) TGA trace and b) DSC curve for HS-liquid.

exothermic peak (T_c). Further increasing the temperature to 20 °C (Figure 2b) should induce melting of the glass phase into the liquid state, giving an evident peak to first-order transition (the corresponding temperature assigned as the melting temperature, T_m). The viscosity of the HS-liquid at 40 °C and 50 °C was determined to be 6.8 Pa·S and 4.2 Pa·S, respectively, very close to the values obtained for sweet honey. Owing to the strong ionic interaction between the OS corona and the PEGS canopy, the liquid-like behavior remained for HS-liquid, even under continual vacuum at 60 °C for more than three months. Such unique solvent-free fluidity with zero vapor pressure offers many opportunities to utilize HS-liquid for target specific applications, such as gas absorption and separation.[4]

The nanostructure of HS-liquid was imaged by scanning electron microscopy (SEM) and TEM. In Figure 3a, well-defined nanospheres are observed in the SEM image, demonstrating that the silica framework is robust and does not collapse during surface engineering. As a result of strong interaction among the surface functional groups, these individual nanoparticles are combined together as large agglomerates. In the TEM image (Figure 3b), monodisperse hollow spheres with approximately 14 nm inner diameter are clearly observed, indicating that the hollow structure is preserved in the liquid state. To further explore if the hollow structure remains empty, a TEM image of a mixture of HS and HS-liquid was recorded. In Figure S4a, there is no difference in contrast between aggregated HS (originating from HS-liquid) and individual HS (from unmodified HS), suggesting that the corona–canopy species remain outside the microporous silica shells. More detailed structural information about the HS-liquid can be obtained from high-resolution TEM images (Figure S4b), which shows empty hollow spheres interconnect to each other by a glue-like polymeric matrix. The elemental mapping of carbon atoms illustrates that these polymeric species built from carbon-containing groups are uniformly distributed in the HS-liquid, functioning as the liquid medium to suspend the hollow spheres (Figure S5). Thus, the hollow structure of silica spheres has been well preserved in liquid-like polymeric medium.

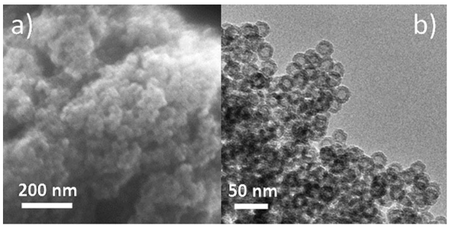

Figure 3. a) SEM and b) TEM images of HS-liquid.

The hollow structure of HS-liquid is further characterized by small-angle X-ray scattering (SAXS) where a nanofluid made from solid SiO_2 spheres (ca. 12 nm) are employed as the reference sample (named as SS-liquid).[9] SAXS curves for the HS- and SS-liquids are shown in Figure 4. As a comparison, SAXS data for the pure hollow and solid spheres are given in Supporting Information. The HS- and SS-liquids clearly have different scattering curves. The SS-liquid is similar to the pure SS powder which had a measured particle size of approximately 11 nm. Similar to the HS powder, the scattering curve for the HS-liquid shows multiple broad peaks indicative of spherical shells, indicating the hollow structure has been preserved.[9]

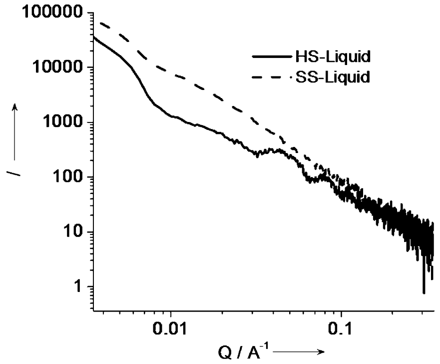

Figure 4. Small-angle X-ray scattering of the HS- and SS-liquid acquired with a 1 h collection time.

Because of the unique chemical and structural properties of the HS-liquid, it is of particular interest for application in gas separation.[4,6a–c] As shown in Scheme 2, benefiting from the chemical structure of the PEG-based polymeric canopy, the HS-liquid exhibits a fluid character with negligible vapor pressure and rather high thermal stability, which enables us to utilize it as a supported liquid membrane for gas separation.[4] Furthermore, the ether groups contained in the canopy

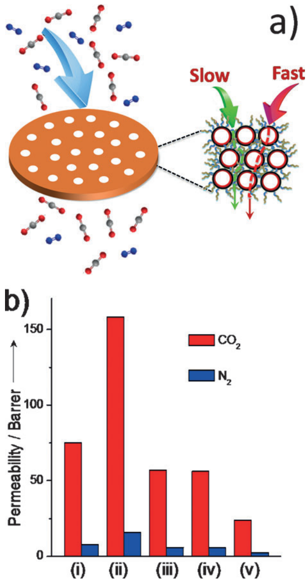

Figure 5. a) Schematic representation of gas separation in membrane supported HS-liquid; b) Gas permeability obtained on i) PEGS, ii) HS-liquid, iii) SS-liquid, iv) CS-liquid, and v) CS/Ni-liquid. The corresponding data of gas separation are summarized in Table S1.

chains, in principle, can enhance the gas solubility and selectivity towards CO_2 via Lewis acid/base interactions, making the HS-liquid a suitable candidate for CO_2 capture.[10] The other advantage of the HS-liquid for gas separation comes from the presence of the empty cavities (Figure 5a), which essentially provide very high fractional free volume to enhance gas diffusivity through the porous liquid.[11] The introduction of hollow structures into a dense polymeric matrix can increase gas diffusivity because the empty cavities essentially provide free space for gas transport, reducing the gas diffusion pathway in the liquid state. To examine this effect, the HS-liquid was supported in a polymeric membrane and the gas separation performance was measured for the separation of CO_2 and N_2 (Figure 5).[12]

In Figure 5b, the CO_2 permeability of the HS-liquid is determined as 158 barrer, higher than the value (75 barrer) obtained for PEGS. However, they have nearly identical CO_2/N_2 selectivity (ca. 10). This experimental finding indicates that the hollow structure indeed can accelerate gas transport in the dense liquid state, while the gas selectivity is still dependent on the organic groups of polymeric chains. To further confirm the enhanced diffusivity, SS-liquid formed from 12 nm solid-sphere cores rather than hollow-sphere cores was employed as a reference sample. As expected, a moderate decrease in the CO_2 permeability (57 barrer) was observed in comparison with PEGS sample, presumably because of the blocking effect of the solid object for gas diffusivity. Furthermore, core–shell (CS) silica spheres with or without nickel-hydrazine cores are used as the building blocks for nanofluid fabrication (the corresponding liquids are named as CS/Ni-liquid and CS-liquid, respectively), with the purpose to exclude the influence of particle size and surface properties for gas separation (Figure S6). In Figure 5b, the CO_2 permeability of CS/Ni-liquid and CS-liquid is determined as 24 barrer and 56 barrer with a similar CO_2/N_2 selectivity (ca. 10), further demonstrating the promotion of empty cavities for gas separation. Hence, a porous liquid with empty cavities is a promising candidate for gas separation.

To conclude, we have demonstrated that surface engineering of hollow silica spheres with suitable corona and canopy species can produce a Type I porous liquid under room temperature. This porous liquid, as expected, can work as a promising candidate for gas separation, by taking advantage of its liquid-like polymeric matrices as a separation medium and the empty cavities as gas transport pathway. However the gas permeability and selectivity are moderately low, the good tunability of this hybrid system affords us ample choices for further optimization. For example, using polymeric chains with task-specific functional groups can enhance both the diffusivity and selectivity towards target gas molecules, thus promoting gas separation. Moreover, such a facile synthetic strategy can be further extended to other types of nanostructure-based porous liquid fabrication, opening up new opportunities for preparation of porous liquids with attractive properties for target specific applications.

Experimental Section

Hollow silica nanospheres (HS): Triblock copolymers F127 (1.0 g; $EO_{96}PO_{70}EO_{96}$, MW = 12000 g mol^{-1}) and 1,3,5-trimethylbenzene (1.00 g) and K_2SO_4 (0.87 g) were dissolved in deionized water (60 mL). The mixed solution was stirred at 13.5 °C for 4 h. Then, tetramethoxysilane (2.43 g) was added to the solution, followed by addition of (3-mercaptopropyl) trimethoxysilane (0.78 g). After stirring at 13.5 °C for 24 h, the mixture was transferred into a Teflon-lined autoclave and aged at 100 °C for 24 h. The precipitate was collected by filtration, washed repeatedly with deionized water, and dried at 100 °C. The as-synthesized sample was calcined in air at 550 °C for 10 h to obtain the silica hollow nanospheres (HS).

HS-liquid: HS (1.0 g) was dispersed in aqueous solution (20 mL; pH ≈ 8–9) and sonicated for 10 min. Then, organosilane (OS; 2.0 mL), $(CH_3O)_3Si(CH_2)_3N^+(CH_3)(C_{10}H_{21})_2Cl^-$, was added to the HS suspension under vigorous stirring. After that, the mixture was aged at room temperature for 24 h. The precipitate collected from the above solution was rinsed three times with water and three times with ethanol, and then dried at 100 °C overnight. The resultant sample, OS@HS, was treated by poly(ethylene glycol) tailed sulfonate (PEGS) solution (15.0 mL, 16.5 %, C_9H_{19}-C_6H_4-$(OCH_2CH_2)_{20}O$-$(CH_2)_3SO_3^-K^+$) at 70 °C for 24 h. The excess of PEGS was extracted by warm toluene 5–6 times, and the aqueous layer was collected and dried (oil bath at 80°C for 12 h). The remaining material from the aqueous layer was dispersed in acetone (15.0 mL), and the clear sol obtained after centrifugation was air-dried at 70 °C for 24 h. The HS-liquid was kept at 60 °C under vacuum for use.

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